

PATENT SPECIFICATION

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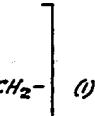
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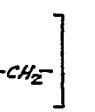
(54) POLYGLYCOL-ETHYLENE-IMINE DERIVATIVES,
 PROCESS FOR THEIR PREPARATION AND THEIR
 USE AS TEXTILE FINISHING AGENTS

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention provides polymers containing recurrent units of the formula



wherein a stands for a number of from 4 to 70, preferably 10 to 50, and recurrent units of the formula



10 in which n represents an integer of from 3 to 11, preferably 5 to 9, and m represents 1 or 2, and having 0.5 to 5 of the fluorine-containing units of the formula (II) per fluorine-free unit of the formula (I).

15 The present invention also provides textile materials finished with these polymers and a process for finishing a textile, which comprises contacting the textile with a solution or dispersion of the polymer according to the invention. Aqueous dispersions are suitable for this purpose as are solutions in inert organic solvents.

15 The present invention also provides a process for preparing the polymer of the invention, which comprises reacting an ethylene imine of the formula



20 where a has the above meaning, with 0.5 to 5 mols of an ethylene imine of the formula



25 in which n and m are defined as above per mol of the ethylene imine of the formula (III), dissolved in an inert organic solvent having a low boiling point and in the

presence of a catalytic amount of boron trifluoride or an aqueous solution of a mineral acid.

The reaction is carried out at a temperature of from 55 to 100° C, preferably at 70 to 90° C.

The molar ratio of the ethylene imines free from fluorine to the fluorinated ethylene imines is between 2 : 1 and 1 : 5, the weight ratio preferably within the limits of 2 : 1 to 1 : 3, particularly to 1 : 2.

The ethylene imines are used as solutions in inert organic solvents having a low boiling point. When operating in an aqueous medium, the solvent is chosen in such a way that it evaporates under the reaction conditions, expediently in such a rate as the solution is added dropwise. As solvents inert towards the ethylene imine derivatives, there may be considered especially fluorinated hydrocarbons or chloro-hydrocarbons of a low molecular weight, particularly those having from 1 to 4 carbon atoms and low-molecular-weight ketones, particularly alkanones having from 3 to 5 carbon atoms, for example, methyl ethyl ketone, methyl isopropyl ketone and particularly acetone.

As polycondensation catalyst there is used boron trifluoride, preferably as a dioxane adduct, or an aqueous mineral acid solution, preferably dilute sulphuric acid, nitric acid, perchloric acid or a hydrohalic acid, especially hydrochloric acid. Hereinafter some preferred operation methods of the preparation process according to invention are described, using preferably hydrochloric acid.

The hydrochloric acid concentration in the reaction mixture advantageously ranges from 0.5 to 5% by weight. In principle, lower or higher concentrations are possible but not advantageous and furthermore require special measures.

It has turned out to be suitable to add to the reaction mixture a polyglycol of the formula



wherein n is a number of from 4 to 70. Preferred are polyglycols having from 10 to 50, particularly from 20 to 50 ethylene glycol units as for example polyglycols with average molecular weights of from 600 to 2000.

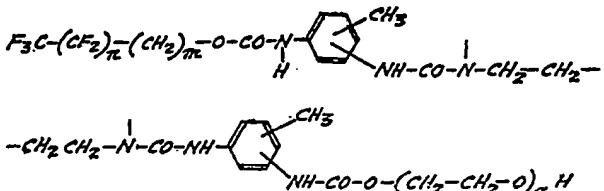
The starting materials for the process according to invention may be obtained as follows:

The ethylene imine derivatives free from fluorine are obtainable by reacting ethylene imine with toluene-diisocyanates, preferably in acetone solution at 0 to 20° C in an atmosphere of inert gas and by reacting the urea derivative so obtained with a polyethylene-glycol having a molecular weight range of from 200 to 3000, preferably of from 1000 to 2000. The reaction of the urea derivative with the polyglycol is expediently carried out at a temperature within the range of from 20 to 40° C.

The fluorine-containing ethylene imines are obtainable by reacting the adducts from fluoroalkanols and toluene-diisocyanates known from French Patent Specification No. 1,438,617 with ethylene-imines. This reaction is advantageously carried out at a temperature within the range of from 0 to 20° C.

A preferred method of operation consists in mixing one part by weight of the compound obtained from the diisocyanate, ethylene-imine and polyglycol and obtained in aceton solution *in situ* with an aceton solution containing 0.5 to 3 parts by weight of the fluorinated ethylene-imine and in adding this mixture dropwise at 70 to 90° C into a solution of hydrochloric acid in water. It is advantageous to add to this bath of hydrochloric acid 1 to 10% by weight, preferably 3 to 6% by weight of a polyethylene-glycol having a molecular weight of from 200 to 3000, preferably 1000 to 2000. There is expediently used the same polyglycol as that bound to the ethylene imine derivative.

By the process of the invention the ethylene-imine ring is opened under the catalytic action of the hydrochloric acid, and a polymerisation of the following components is initiated:



The employed solvent evaporates within the mentioned temperature range and may be reintegrated into the process after recovery.

The polymers are obtained as colourless, aqueous stable dispersions, the active ingredient content of which preferably ranges between 10 and 30%. The solids content remaining constant, viscosity of the dispersion increases in dependency on the hydrogen chloride concentration. When the concentration in the bath amounts to 0.5 to 1% of hydrochloric acid, low-viscous emulsions are obtained, whereas concentrations of 3 to 5% of hydrochloric acid result in viscous, gel-like pastes which are thixotropic.

The resulting concentrated dispersions may easily be diluted to, for example, 1% of active ingredient by introducing while stirring into water or by addition of water.

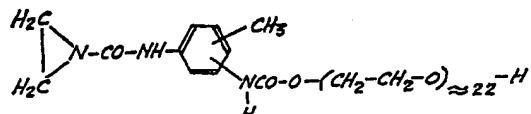
15 It is also possible to start the reaction in anhydrous inert organic solvents with boron trifluoride. The products are generally obtained in form of solids. A solution of such a solid in a low-molecular-weight ketone, preferably an alkanone having from 3 to 5 carbon atoms, for example methyl-ethyl ketone and particularly acetone, or in a mixture of a low-molecular-weight fluorinated hydrocarbon or chloro-hydrocarbon, preferably having from 1 to 4 carbon atoms, and a low-molecular-weight alcohol, preferably having from 1 to 4 carbon atoms, especially a mixture of 1,1,2-trifluoro-1,2,2-trichloro-ethane and isopropanol, is highly suitable for textile finishing. These mixtures have the advantage that they may easily be sprayed.

20 The molar ratio of the ethylene-imine derivatives free from fluorine to those containing fluorine is expediently such that the fluorine content of the active ingredient ranges between 10 and 30%.

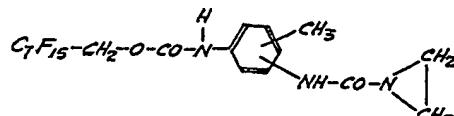
The preparation process according to invention and the excellent properties of the products so obtained are illustrated by the following Examples and test results.

Example 1

14 g (0.08 mol) of toluene-diisocyanate (essentially 2,4-isomer) were dissolved in 100 ml of acetone and mixed under an atmosphere of nitrogen with 3.5 g (0.08 mol) of ethylene-imine at 10 to 20° C. 80 g (0.08 mol) of polyethylene-glycol having a molecular weight of 1000 were introduced while stirring into this solution at 30 to 40° C. A solution of the product having the formula



was obtained which was mixed with a solution of 100 g (0.15 mol) of the fluorinated ethylene-imine having the formula



35 (obtained from equimolar amounts of toluene-diisocyanate (essentially 2,4-isomer), 1,1-dihydroperfluoro-octanol-(1) and ethylene-imine) in 100 ml. of acetone

40 For polymerisation, this mixture was added while stirring vigorously at 70 to 90° C within 4 hours into an aqueous bath containing 600 ml of H_2O , 8 ml of 35% hydrochloric acid and 18 g of polyethylene-glycol having a molecular weight of about 1000. At the mentioned polymerization temperature, 195 ml of acetone distilled off continuously at the rate of dropwise addition of solution. When the reaction was completed, a low-viscous dispersion was obtained having a solids content of 26%, the fluorine content of the active ingredient being 22% and the pH-value about 1.

Example 2

45 The reaction was carried out as described in Example 1, using the following amounts: 21 g (0.13 mol) of toluene-diisocyanate, 5.5 g of ethylene-imine (0.13 mol), 130 g (0.13 mol) of polyethylene-glycol having a molecular weight of about 1000 and 75 g (0.11 mol) of the fluorinated ethylene-imine. These substances were added as described above to an aqueous bath (690 ml of H_2O , 15 ml of 35% hydrochloric acid and 21 g of polyethylene-glycol of a molar weight of about 1000). A dispersion was obtained with an active ingredient content of 26.4%, the fluorine content of which was 13.7%.

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Example 3

The reaction was carried out as described in Example 1, using the following amounts: 14 g (0.08 mol) of toluene-diisocyanate, 3.5 g (0.08 mol) of ethylene-imine, 50 g (0.08 mol) of polyethylene-glycol having a molar weight of about 1000 and 200g (0.3 mol) of the fluorinated ethylene-imine. These substances were added as described above to an aqueous bath (900 ml of H_2O , 30 ml of 35% hydrochloric acid and 27 g of polyethylene-glycol having a molecular weight of about 1000). A dispersion having an active ingredient content of 26%, was obtained, the fluorine content of which was 28.5%.

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Example 4

The reaction was carried out as described in Example 1, using the following amounts: 11.4 g (0.066 mol) of toluene-diisocyanate, 2.85 g (0.066 mol) of ethylene-imine, 136 g (0.066 mol) of polyethylene-glycol having an average molecular weight of 2060 and 150 g (0.22 mol) of the fluorinated ethylene-imine. These substances were introduced as described above into an aqueous bath (900 ml of water, 30 ml of 35% hydrochloric acid and 54 g of polyethylene-glycol of a molecular weight of 2060). A dispersion having an active ingredient content of 27.5%, was obtained, the fluorine content of which was 19.5%.

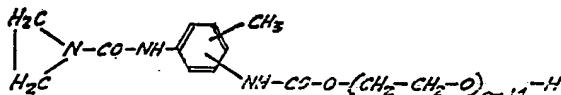
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Example 5

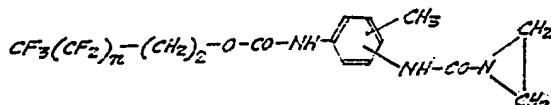
13.6 g (0.078 mol) of commercial toluene-diisocyanate (essentially 2,4-isomer) were dissolved in 100 ml of acetone and mixed under an atmosphere of nitrogen with 3.4 g (0.078 mol) of ethylene-imine at 10 to 20° C. 47 g (0.078 mol) of polyethylene-glycol having a molecular weight of 600 were introduced while stirring into this solution at 30 to 40° C.

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A solution of the product having the formula



was obtained, which was added to a solution of 65.2 g (0.158 mol) of a fluorinated ethylene-imine mixture of the formula



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$n=7.5$

(as an average value from $n=5, 7$ and 9 in the ratio mentioned below)
(obtained from equimolar amounts of toluene-diisocyanate (essentially 2,4-isomer), a mixture of fluorinated alcohols consisting of

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21.8% of $n-C_4F_{13}(CH_2)_2 OH$
56.8% of $n-C_8F_{17}(CH_2)_2 OH$ and } (average molecular
21.4% of $n-C_1_1F_{21}(CH_2)_2 OH$ } weight 413.5)

and ethylene-imine) in 100 ml of acetone.

For polymerization this mixture was added while stirring vigorously at 70 to 80° C within 3 hours into an aqueous bath which consisted of 400 ml of H_2O , 6 ml of HCl (35%) and 15 g of polyethylene-glycol having a molecular weight of about 1000.

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At the mentioned polymerization temperature 195 ml of acetone distilled continuously off at the rate that the solution was added dropwise. When the reaction was completed a low viscous dispersion was obtained having a solids content of about 26%, the fluorine content of which was 15.4%.

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TEST METHODS AND RESULTS

Textiles (polyethylene-glycol-terephthalate and cotton) finished with the aqueous dispersions according to this invention obtained as described in the following examples, were pre-treated for test purposes for:

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oil—and water repellency
fastness to solvents and
soil release capacity
according to the following method:

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The fabric samples were submerged into aqueous dispersions of active ingredients and then squeezed off. The highly concentrated dispersions of the new fluorinated products were diluted with water to an active ingredient content of 1%. The submerged and dried fabric samples were exposed for 5 minutes to a thermal after-treatment at 150° C. The active ingredient pick-up was 0.9 to 1%, calculated on the fabric weight. 5

The oil-repellency of the fabrics finished in this way was tested with *n*-heptane-paraffin oil mixtures according to the scale of values given in U.S. Patent Specification No. 3,362,782:

Oil repellency value	% by volume of <i>n</i> -heptane	% by volume of paraffin oil DAB 6*
50	0	100
60	10	90
70	20	80
80	30	70
90	40	60
100	50	50
110	60	40
120	70	30
130	80	20

*DAB = Deutsches Arzneibuch

In order to test water repellency (water-repellent effect) water drops were applied with a pipet on the material to be tested and the effect was judged after a period of 3 minutes using the following characteristics:

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- + no wetting
- ± slight wetting
- immediate wetting.

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For testing the fastness to washing of the soil release finishing, the samples were washed with a commercially available detergent up to 5 times at 100° C.

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For testing the soil release capacity, two types of soiling deposits were used:

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- a) soiled motor oil
- b) olive oil and 1% by weight of the dyestuff Colour Index No. 26100.

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The separately applied soiling deposits for test purposes were contacted for 15 minutes at 25° C with the textile samples finished with the chemicals according to invention (size of the samples 7 x 7 cm; amount of the soiling deposits 0.1 ml). After being covered with glass the soiled fabric samples were exposed for 30 minutes to a pressure of 1 kg/49 cm² and subsequently aged for one hour at 80° C in a drier. Then the fabric samples were washed at 100° C with a commercially available detergent, and the washing resistance of the soil was determined.

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For testing the fastness to washing of the soil release finishing, the samples were washed 5 times and then soiled.

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On the basis of these test methods the products according to this invention were examined on polyethylene terephthalate and cotton and compared with a commercial product. The results are listed in the Table below. They were determined by coating with 1% of active substance, calculated on the fabric weight.

TABLE

Oil- and water-repellency	polyethylene terephthalate Example 1	Cotton : Example					Commercial* + product
		1	2	3	4	5	
not washed	110+	120+	100+	100+	110+	110+	90+
washed 1x	110+	100+	100+	100+	100+	70-	70-
washed 2x	110+	100+	90+	90+	90+	70-	70-
washed 5x	110+	90+	90+	80+	90+	0	0--
soil release capacity	good	very good	good	very good	very good	good	good
resistance to washing	very good	very good	good	good	good	good	moderate

* Commercial product FC 218 of 3-M Company.
See previously for explanation of the symbols + and -.

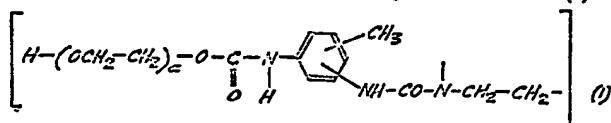
Transactions

Example 6 50 g (0.075 mol) of an addition product consisting of equimolar amounts of cyclohexene-diisocyanate (essentially 2,4-isomer), *n*-1,1,2,2-tetrahydro-perfluorodecanol-(4), and ethylene-imine and 50 g (0.042 mol) of an addition product of equimolar amounts of the above diisocyanate, polyethylene-glycol having a molar weight of 1000 and diethylene-imine, were heated in 100 g of acetone, resulting in a nearly complete solution of the compounds. This solution was mixed with 0.5 g of BF_3 -dioxane and maintained for 5 hours at 50° C. After the acetone had been eliminated, a slightly yellow and sticky powder was obtained which was easily soluble in acetone and mixtures of 1,1,1,2,2,2,2-trifluoro-1,2,2,2-trichloroethane with isopropanol.

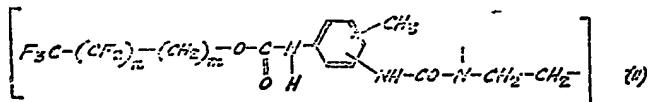
A blended fabric of polyethylene terephthalate and cotton (50 : 50) was sprayed with a solution of the before mentioned polymer in 1,1,2-trifluoro-1,2,2-trichloroethane/isopropanol (1 : 1), so that the pick-up of fluorine was 0.2%, calculated on the fabric weight. Then the fabric was fixed for 5 minutes at 150° C. The so finished fabric showed an initial oil repellency value of from 110 to 120.

With a fluorine coating of 0.1% obtained in analogous way, an initial oil repellency value of 80 had already been obtained.

WHAT WE CLAIM IS:—

1. A polymer containing recurring units of the general formula (I)5 in which a stands for a number of 4 to 70, and recurring units of the general formula (II)

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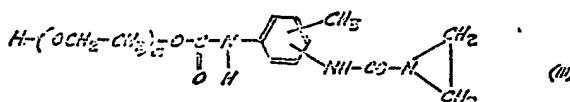
In which n stands for a number of 3 to 11 and m for 1 or 2, the ratio of the units of formula (I) to the units of formula (II) being 1 : 0.5 to 1 : 5.10 2. The polymer as claimed in claim 1, wherein n stands for a number of 5 to 9.

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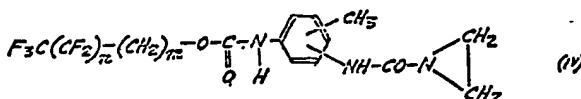
3. The polymer as claimed in claim 1 or claim 2, wherein a stands for a number of 10 to 50.

4. A process for the preparation of a polymer containing recurring units of the general formulae (I) and (II) given in claim 1, which comprises reacting 1 molar proportion of a compound of the general formula (III)

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in which a is as defined in claim 1, with 0.5 to 5 molar proportions of a compound of the general formula (IV)

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in which n and m are as defined in claim 1 per mol of the compound of formula (III), in an inert organic solvent at a temperature in the range of 55° C to 100° C with a catalytic amount of boron trifluoride or an aqueous mineral acid.

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5. A process as claimed in claim 4, wherein the temperature is 70 to 90° C.

6. A process as claimed in claim 4 or claim 5, wherein the inert organic solvent is an alkanone containing 3 to 5 carbon atoms or a fluorinated hydrocarbon or chloro-hydrocarbon containing 1 to 4 carbon atoms.

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7. A process as claimed in claim 4 or claim 5, wherein the inert organic solvent is acetone.

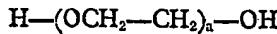
8. A process as claimed in any one of claims 4 to 7, wherein the mineral acid is sulphuric acid, perchloric acid, nitric acid or a hydrohalic acid.

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9. A process as claimed in any one of claims 4 to 7, wherein the mineral acid is hydrochloric acid.

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10. A process as claimed in any one of claims 4 to 9, wherein as an adjuvant a polyethylene glycol of the general formula



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in which a is a number of 4 to 70, is used.

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11. A process as claimed in claim 10, wherein a polyethylene glycol is used, the value a of which is the same as that of the compound of the general formula (III).

12. Any process for the preparation of a polymer as claimed in claim 1, conducted substantially as described herein or in the Examples.

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13. A polymer as claimed in claim 1, whenever prepared by a process as claimed in any one of claims 4 to 12.

14. A process for rendering a textile oil- and water-repellent, which comprises contacting said textile with a solution or dispersion of a polymer containing recurring units of the general formulae (I) and (II) given in claim 1.

15. A process as claimed in claim 14, wherein an aqueous dispersion of said polymer is used.

16. A process as claimed in claim 14, wherein a solution of said polymer in an inert organic solvent is used.

5 17. A process as claimed in claim 16, wherein a solution of said polymer in an alkanone containing 3 to 5 carbon atoms or a mixture of an alkanol containing 1 to 4 carbon atoms and a fluorinated hydrocarbon or chlorohydrocarbon containing 1 to 4 carbon atoms is used.

10 18. A process as claimed in claim 17, wherein a solution of the said polymer in acetone or in a mixture of isopropanol and 1,1,2-trifluoro-1,2,2-trichloroethane is used.

19. A process as claimed in claim 18, wherein a solution of the said polymer in acetone or in a mixture of isopropanol and 1,1,2-trifluoro-1,2,2-trichloroethane is sprayed on the said textile, which is thereafter submitted to a heat treatment.

15 20. Any process for the finishing of a textile according to claim 14, conducted substantially as described herein or in the Examples.

21. A textile material whenever treated according to a process as claimed in any one of claims 14 to 20.

22. A textile material whenever finished with a polymer as claimed in any one of claims 1 to 3 and 13.

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